

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Simultaneous Polymerization and Alkylation of Heterocyclic N-Vinyl Monomers

We, GENERAL ANILINE & FILM CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America of 140 West 51st Street, New York, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and 10 by the following statement:—

This invention relates to a new process of simultaneously polymerizing and alkylating heterocyclic N-vinyl monomers whereby a range of polymers is obtained having solubility in a wide range of solvents, from polar to non-polar, and to a new and useful class of such polymers.

It is known that homopolymers of heterocyclic N-vinyl lactams, N-vinyl oxazolidones, N-vinyl morpholinones, etc. and copolymers thereof with other monomers containing a polymerizable vinyl group can be readily prepared by conventional procedures. Homopolymers of such heterocyclic N-vinyl monomers and copolymers thereof containing from 1% to 95% by weight of a monomer having a polymerizable vinyl group are generally soluble in a wide variety of different solvents such as alcohols, ether-alcohols, amines, and other polar organic solvents, but insoluble in aliphatic hydrocarbons such as hexane, heptane, cyclohexane, methylcyclohexane, mineral spirits, mineral oil, lubricating oil, and other non-polar organic solvents.

Commercial requirements have arisen for homopolymers and copolymers of heterocyclic N-vinyl lactams, N-vinyl oxazolidone, N-vinyl morpholinone, which possess the characteristics imparted by the presence of their heterocyclic rings but which have special solubility characteristics that are dictated by the particular end use in view. For ex-

ample, polyvinylpyrrolidone, and copolymers of vinylpyrrolidone and vinyl acetate, are very effect as hair grooming aids, but for certain applications their solubility in water is undesirable and a lower degree of hygroscopicity and an increased moisture resistance would be desirable. In another instance, the effectiveness of polyvinylpyrrolidone as a dispersing agent cannot be utilized because it is insoluble in the medium, such as a lubricating oil, in which it is to function as a dispersant. The same applies to polyvinylimidazole, polyvinyloxazolidones and polyvinylmorpholinones. In another instance, the adhesive properties imparted to the polymer by the heterocyclic ring are partly vitiated because of poor moisture resistance. A further example is the inability to utilize the complexing ability of such homopolymers and copolymers as dye receptors in difficult-to-dye resins such as polyethylene and polypropylene because of the insolubility of the polymers in such resins.

It is the object of the present invention to provide a new process of simultaneously polymerizing and alkylating heterocyclic N-vinyl monomers alone, a mixture of two different heterocyclic N-vinyl monomers, or a mixture of a heterocyclic N-vinyl monomer and a non-heterocyclic polymerizable mono-ethylenically unsaturated monomers so as to systematically control the solubility of the alkylated polymers. Thus, by the proper choice of alkylating agent and the degree of alkylation, it is possible to prepare polymers which are soluble in polar solvents, such as alcohols, but which are much less sensitive to moisture, or polymers which are soluble in aliphatic hydrocarbons of from 6 to 60 carbon atoms including isomers thereof, mineral and lubricating oils having a Saybolt viscosity of from 50 to 200 seconds,

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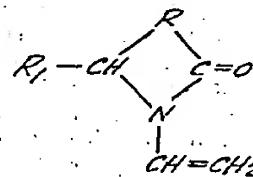
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or polymers having intermediate degrees of solubility between polar and non-polar solvents. This systematic control of the solubility characteristics of the polymer is achieved without destroying the other desirable characteristics imparted by the heterocyclic ring, and thus polymers can be prepared which overcome the deficiencies described above.

10 We have found that heterocyclic N-vinyl monomers are readily polymerized and alkylated by treating one mole of such monomer alone, or one mole of a mixture of two such monomers, or one mole of a mixture containing such monomer and a non-heterocyclic polymerizable monoethylenically unsaturated monomer with 0.05, to 12 moles of an α -olefin in solution of an organic solvent common to the monomer, or mixture of monomers and the α -olefin in the presence of 0.025 to 0.30 mole of an organic peroxide catalyst per mole of α -olefin at a temperature ranging from 80° to 200°C. for a period of time ranging from 3 to 60 hours. The resulting solution of polymerized and alkylated polymer may be employed as such or, if desired, the organic solvent may be removed by vacuum distillation. The degree of alkylation is determined by the amount of the α -olefin consumed and may range from as low as 1% to 90% by weight of the alkylated polymer. The solubility in polar solvents decreases and the solubility in non-polar solvents increases as the degree of alkylation increases. In other words, homopolymers and copolymers, may be obtained in which some or all of the heterocyclic rings contain one or more alkyl groups of at least 2 carbon atoms. The average molecular weight of such homopolymers and copolymers varies from 50,000 to 350,000.

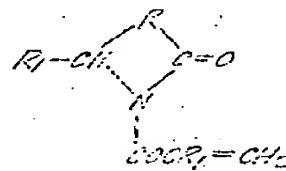
40 The heterocyclic N-vinyl monomers which are simultaneously polymerized and alkylated with an α -olefin in accordance with the present invention may be characterized by the following general formulae:



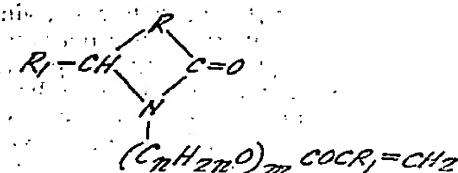
wherein R represents an alkylene bridge group, i.e., $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ and $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ to complete a 5, 6 and 7-membered heterocyclic ring system (lactam) respectively and R₁ represents either a hydrogen atom or a methyl group, which will include N-vinyl-2-pyrrolidone, N-vinyl-5-methyl-2-pyrrolidone, N-vinyl-2-piperidone, N-vinyl-6-methyl-2-piperidone, N-vinyl-7-methyl caprolactam.

lactam and N-vinyl-7-methyl caprolactam. Comparable compounds are available from the corresponding thiolactams and these can be used in the process of this invention.

Another group of heterocyclic vinyl-monomers comprises N-vinyl oxazolidone, N-vinyl succinimide, N-vinyl piperidine, N-vinyl di-glycolimide, N-vinyl glutarimide, N-vinyl-3-imidopholinone; amides obtained by the reaction of a 5-, 6- or 7-membered lactam with acryloyl or methacryloyl chloride or bromide in the presence of a hydrogen halide acceptor such as pyridine, dimethyl-aniline, having the structure



wherein R and R₁ have the same values as above. Illustrative compounds are N-methacryloyl-pyrrolidone, -piperidone and -caprolactam, N-methacryloyl-5-methyl-pyrrolidone, N-methacryloyl-6-methyl-piperidone and N-methacryloyl-7-methyl caprolactam, N-acryloyl-pyrrolidone, -piperidone and -caprolactam, N-acryloyl-5-methylpyrrolidone, N-acryloyl-6-methylpiperidone and N-acryloyl-7-methyl caprolactam, acrylic esters having the structure



wherein R and R₁ have the same values as above, m is an integer of from one to four inclusive, and n is an integer of from one to four inclusive when m has a value of one and from two to four inclusive when m has a value greater than one. Illustrative compounds are N-acryloxymethyl-pyrrolidone, -piperidone and -caprolactam, N-methacryloxyethyl-pyrrolidone, -piperidone and -caprolactam; N-methacryloxy-propyl-pyrrolidone, -piperidone and -caprolactam; N-methacryloxymethyl-pyrrolidone, -piperidone and -caprolactam; N-methacryloxyethyl-pyrrolidone, -piperidone and -caprolactam; N-methacryloxyethyl-5-methylpyrrolidone, -6-methylpiperidone and -7-methylcaprolactam, including amidoalkyl lactams of the structure

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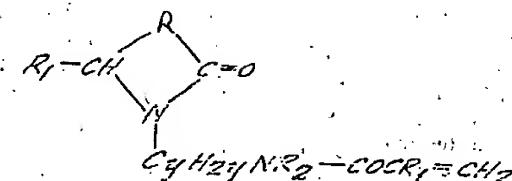
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wher cin R and R₁ have the same value as above, R₂ represents a hydrogen atom, an alkyl group of from 1 to 12 carbon atoms inclusive or phenyl, and y is 2 or 3. Illustrative compounds of this type are N - methacrylamidomethyl -, N - methacrylamido - ethyl -, N - methacrylamidopropyl - and N - (N - phenylacrylamidopropyl) - pyrrolidones, - piperidones and - caprolactams, which are readily prepared by reacting acryloyl or methacryloyl chloride or bromide with an N - (aminoalkyl) - lactam, wherein the alkyl is from 1 to 12 carbon atoms inclusive, in the presence of any conventional base to take up the hydrogen halide.

In the simultaneous polymerization and alkylation of a mixture of comonomers containing from 5% to 99% by weight of any one of the foregoing heterocyclic N-vinyl monomers and from 1% to 95% by weight of a non-heterocyclic polymerizable monoethylenically unsaturated monomer, the procedure is exactly the same as that employed for the heterocyclic N-vinyl monomers alone or a mixture of two such monomers. The various non-heterocyclic polymerizable monoethylenically unsaturated monomers which may be copolymerized with the heterocyclic N-vinyl monomers, include vinyl acetate, vinyl methoxy-acetate, vinyl diethylacetate, vinyl trimethylacetate, vinyl propionate, vinyl isobutyrate, vinyl butyrate, vinyl lactate, vinyl caproate, vinyl caprylate, vinyl stearate, acrylic and methacrylic monomers such as methyl methacrylate, cyclohexyl methacrylate, isobutyl methacrylate, isooamyl methacrylate, β -methoxy ethyl methacrylate and α - (α - chlorophenyl) ethyl methacrylates, β -phenoxyethyl methacrylate, β -phenylethyl methacrylates, phenyl methacrylate, *o*-cresyl methacrylate, *p*-cyclohexylphenyl methacrylate, 2 - nitro 2 - methyl propyl methacrylate, diethylaminoethyl methacrylate, ethylidene acetate methacrylate and glycidyl methacrylate, including esters of halo acrylic acids, such as methyl- α -chloro-acrylate, ethyl - α - chloro acrylate, phenyl - α - chloro - acrylate, α - ethylacrylic acid, methyl acrylate, propyl acrylate, acrylic acid, methacrylic acid, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, as well as N-alkyl and N-aryl substituted acrylamides. For the purpose of the present invention, the nature or character of the non-heterocyclic polymerizable monoethylenically unsaturated monomer is immaterial so long as such monomer is capable of copolymeriza-

tion in any proportion with the heterocyclic N-vinyl monomer.

It is to be noted that a mixture of comonomers containing as low as 5% by weight of a heterocyclic N-vinyl monomer and 95% by weight of a non-heterocyclic polymerizable monoethylenically unsaturated monomer will contain sufficient nitrogen containing heterocyclic rings for alkylation during the simultaneous polymerization and alkylation reaction.

It is to be further noted that in lieu of such a mixture, a mixture of two different heterocyclic N-vinyl monomers may be employed. The latter mixture may contain from 5% to 99% by weight of any one of the aforementioned heterocyclic N-vinyl monomers and from 1% to 95% by weight of another heterocyclic N-vinyl monomer. Such a comonomer mixture will contain ample nitrogen containing heterocyclic rings for a higher degree of alkylation during the simultaneous polymerization and alkylation reaction.

Any α -olefin having a molecular weight from 28 to as high as 2500 may be employed in the alkylation of monomers of the above heterocyclic N-vinyl compounds, alone or in admixture during the simultaneous polymerization and alkylation reaction. In other words, α -olefins ranging from ethene, propene, 1-butene, 1-pentene, 2-ethyl-1-butene, 2-methyl-1-pentene, 1-hexene, 5-methyl-1-hexene, 2-methyl-1-pentene, 3-ethyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 2-ethyl-1-hexene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-cicosen, 1-docosene, 1-tetraacosene, 1-pentacosene and polybutenes of molecular weight of 400 to 2500 may be employed.

Instead of employing any one of the foregoing individual α -olefins, a mixture of commercially available linear α -olefins produced by cracking petroleum wax or by polymerizing lower olefins may also be used as the alkylating agent. The commercial product composition contains a mixture of linear olefins. Such mixture may contain linear olefins ranging from 6 to 8 carbon atoms, 8 to 10 carbon atoms, 10 to 12 carbon atoms, 12 to 16 carbon atoms, 16 to 20 carbon atoms and as high as 20 to 42 carbon atoms. For example, the product composition of linear heptene having 92% of mono-olefins, contains 89% of α -heptene, 6% of α -hexene and 5% of α -octene based on the mono-olefin basis. By careful distillation of the commercial product composition substantially individual α -olefins are obtained which may be used as the alkylating agent.

While linear α -olefins are preferred because of their commercial availability, we have found that the numerous isomers of α -olefins ranging from 1-pentene to 1-pentacosene as

well as polybutenes may also be employed in the alkylation reaction. The only precaution required in such case is that the isomer contain an ethylenic unsaturation in the α -position thereof.

Instead of employing ethylene (ethene) as the alkylating agent, chloro-fluoro α -olefins such as for example dichlorovinylidene fluoride ($\text{CCl}_2=\text{CF}_2$), chlorovinylidene fluoride ($\text{CHCl}=\text{CF}_2$), chlorotrifluorovinylene ($\text{CClF}=\text{CF}_2$) tetrofluoroethylene ($\text{CF}_2=\text{CF}_2$), vinylidene fluoride ($\text{CH}_2=\text{CF}_2$) may be used to yield a series of new and useful polymers containing on the nitrogenous heterocyclic ring a fluoro or chlorofluoro ethane group.

In carrying out the simultaneous polymerization and alkylation reaction, an organic solvent common to the α -olefins; fluoro- α -olefins; chloro-fluoro- α -olefins, the heterocyclic N-vinyl monomer alone, a mixture of two different heterocyclic N-vinyl monomers, or a mixture of a heterocyclic N-vinyl monomer and a non-heterocyclic polymerizable monoethylenically unsaturated monomer is employed. As solvents it has been found that various alcohols such as methanol, ethanol, propanol, isopropanol, butanol, sec-butanol, amyl alcohol, hexanol, 2-ethyl-1-hexanol, ethylene glycol, 1,2-butanediol, 1,4-butanediol, are very effective. Other solvents such as diacetone alcohol, diethylene glycol, ethylene glycol monomethyl ether acetate, methylene chloride may also be employed. It is to be noted that the nature or character of the organic solvent is immaterial so long as it is a liquid, forms a solution with the heterocyclic N-vinyl monomers and polymers, the non-heterocyclic polymerizable monoethylenically unsaturated monomers and copolymers, the α -olefin and the fluoro and chloro-fluoro derivatives thereof and is less susceptible to alkylation than the aforementioned monomers and polymers.

The amount of organic solvent employed is not critical. Any amount which will yield a solution of the monomer, mixture of monomers, and α -olefin or the fluoro or chloro-fluoro derivatives thereof will suffice. However, for purposes of expediency, we found that for every part by weight of monomer, or a mixture of monomers from 2 to 10 parts of organic solvent either by volume or by weight, are sufficient to yield a workable solution.

As a peroxide catalyst (initiator) for the polymerization and alkylation reaction we can employ any one of the known organic peroxides normally employed as initiators in chemical reactions such as, for example, t-butyl - perbenzoate, di - benzoyl peroxide benzoyl hydperoxide, t-butyl hydroperoxide, t-butyl perphthalic acid, *p*-chlorobenzoyl peroxide, t-butyl peracetate, di-t-butyl peroxide, cumene peroxide.

Where homopolymers and copolymers of

a low degree of alkylation are desired, and a low molecular weight α -olefin is used, the simultaneous polymerization and alkylation reaction may be conducted in the presence of any one of the aforementioned alcohols.

Where it is desired that the alkylated homopolymer or copolymer be soluble in an aliphatic liquid hydrocarbon of 6 or more carbon atoms, a mineral oil or lubricating oil of a paraffinic stock is used. The simultaneous polymerization and alkylation reaction is preferably conducted in the presence of a higher boiling aliphatic alcohol such as for example hexanol. When the desired degree of alkylation has been obtained the reaction mixture is subjected to vacuum distillation and the higher boiling alcohol is removed and replaced by a saturated aliphatic hydrocarbon having a boiling point higher than the alcohol. After the alcohol has been removed there is obtained a solution of the alkylated polymer in solution of the aliphatic hydrocarbon. Saturated aliphatic hydrocarbons having a boiling point higher than hexanol are legion and commercially available. Hence, no difficulty should be encountered in the selection of such hydrocarbon in preparing a solution of the alkylated homopolymer or copolymer.

The only deviation from the foregoing procedure is where low-boiling α -olefins of from 2 to 6 carbon atoms inclusive and the fluoro- and chloro-fluoro α -olefins are employed as the alkylating agents. In such case the organic peroxide catalyst, preferably di-t-butyl peroxide, and the solution of the heterocyclic N-vinyl monomer or a mixture of monomers are introduced into a stainless steel rocker bomb. The low-boiling α -olefin or fluoro- or chloro-fluoro α -olefin is then charged into the bomb and the bomb heated and maintained at a temperature of from 110° to 140°C. for a period of time ranging from 5 to 28 hours. The pressure developed in the bomb may range from 100-1000psi. After cooling to room temperature the contents of the bomb are discharged into any suitable vacuum distillation equipment to remove the solvent and the residual product recovered as a solid.

The following examples will show how the various heterocyclic N-vinyl monomers, alone or in admixture with other polymerizable monomers, are simultaneously polymerized and alkylated. All parts given are by weight unless otherwise noted.

For the sake of simplicity, the lubricating oil of paraffinic stock having a Saybolt viscosity of 100 seconds marketed by the Secony Mobil Oil Co. as "100 sec. solv." will be referred to hereinafter as "100 sec. solvent".

EXAMPLE I

Into a one-liter, four-necked flask, equipped with stirrer, thermometer, nitrogen inlet and

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reflux condenser, the following ingredients were charged:

N-vinyl-2-pyrrolidone, 111 grams (1.0 mole)

α -eicosene, 140 grams (0.5 mole)

5 methyl *isobutyl* carbinol, 200 grams

di-*t*-butyl peroxide, 7.3 grams (0.05 mole)

The flask was then purged with nitrogen and heated. When the reaction temperature

reached around 120°C. an exothermic re-

action initiated, but the temperature was con-

trolled and maintained at 120°—135°C. After

16 hours of reaction, the experiment was dis-

continued and the contents analyzed. The

results showed the absence of any N-vinyl-

2-pyrrolidone and 2.73% of α -eicosene, cor-

responding to only 12.5 grams of the olefin

charged. The product after the total removal

of the solvent was a waxy solid at room

temperature.

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EXAMPLE II

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following ingredients

were charged and the flask then purged with

25 nitrogen and heated:

N-vinyl-2-pyrrolidone=83.2 grams (0.75 mole)

α -dodecene=126 grams (0.75 mole)

normal butanol=150 grams

30 di-*t*-butyl peroxide=11 grams (0.075 mole)

The contents of the flask were maintained

at 120°—125°C. for 12 hours when a second

charge of peroxide (5.5 grams, 0.037 mole)

was introduced and the reaction continued

35 for another 12 hours. (Total peroxide=16.5

grams, or 0.11 mole). The solution was

analyzed and found to contain no residual N-

vinyl-2-pyrrolidone and only 2.26% by

40 weight of α -dodecene corresponding to 8.5

grams of the unreacted olefin. The contents

of the flask were then transferred into a

one-liter flask and the solvent stripped in

high vacuum. The resulting product was a

colourless flexible solid, strongly hydro-

45 phobic.

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EXAMPLE III

Into a one-liter, four-necked flask equipped

with stirrer, thermometer, nitrogen inlet and

reflux condenser, the following ingredients

were charged and the system purged with

50 nitrogen:

N-vinyl-2-pyrrolidone, 37 grams (0.33 mole)

α -dodecene, 336 grams (2.0 mole)

normal butanol, 200 grams

55 di-*t*-butylperoxide, 14.6 grams (0.1 mole)

The contents were brought to reflux

(120°—125°C.) and maintained for 24 hours

and then another 14.6 grams (0.1 mole) di-

56 *t*-butyl peroxide was added and heating con-

tinued for 24 more hours. (Total peroxide

used=29.2 grams or 0.2 mole). The con-

tents were then cooled and analyzed. It

was found to contain no residual N-vinyl-2-

pyrrolidone and only 4.65% α -dodecene, corresponding to 28 grams of the olefin charged. The product obtained after the removal of all the volatiles in high vacuum, was colourless and viscous fluid soluble in most organic solvents.

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EXAMPLE IV

70 Into a one-liter stainless steel shaker bomb, a prepared solution of 111 grams (1.0 mole) N-vinyl-2-pyrrolidone, 200 grams ethanol and 25 grams (0.17 mole) di-*t*-butyl peroxide was charged and then the bomb capped and 140 grams of ethylene injected and the bomb sealed. The bomb was heated and maintained at 125—130°C. with shaking for 24 hours. It was then cooled, vented and the contents discharged into a stainless steel pan and placed in vacuum oven. After a continuous drying period of two days at 90°C. (20—30 mm. of mercury) the dried product was analyzed and found to contain no N-vinyl pyrrolidone but 6.8% nitrogen, corresponding to 54% reacted N-vinyl-2-pyrrolidone in the product. The product was a light brown transparent semisolid and non-tacky to a wet finger.

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EXAMPLE V

126 Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following ingredients were charged and the system then purged with nitrogen:

N-vinyl-2-pyrrolidone=111 grams (1.0 mole)

α -eicosene=280 grams (1.0 mole)

methyl *isobutyl* carbinol=200 grams

di-*t*-butyl peroxide=14.6 grams (0.1 mole)

The contents were maintained at 130°—

135°C. for 16 hours and then a second addi-

tion of 7.3 grams (0.05 mole) peroxide was

made and reaction continued for 8 more

hours. (Total peroxide=21.9 grams, 0.15

mole). The solution was cooled and analyzed.

The analytical data showed the total absence

of N-vinyl-2-pyrrolidone and only 5.48%

α -eicosene, corresponding to 33.6 grams of

the olefin. The contents were subjected to

vacuum distillation and as the solvent was

removed 391 g. 100 Sec. Solv. was added.

At completion, a clear viscous fluid weighing

780 grams was obtained. On cooling to room

temperature the product concentrate turned

to a waxy solid, but became a clear fluid

on warming.

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methyl *isobutylcarbinol*=200 grams
di-*t*-butyl peroxide=15 grams (0.1 mole)

After a thorough purge with nitrogen the contents were heated. At about 105°C. of pot temperature, a vigorous reflux of vinyl acetate (B.P. 72-73°C.) was observed and the temperature slowly increased as the refluxing decreased. The contents were maintained at 120°-135°C. for 16 hours and then 10.0 grams of the peroxide were added and the reaction continued for another 8 hours. (Total peroxide=25.0 grams or 0.17 mole). The analysis of the solution showed the total absence of N-vinyl-2-pyrrolidone, the presence of 0.07% vinyl acetate (equiv. to 0.5 gram) and only 3.3% of α -hexadecene equivalent to 23.5 grams of the olefin. The product, after the removal of the solvent, was a relatively transparent solid soluble in 100 Sec. Solv.

EXAMPLE VII

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following materials were charged:

N-vinyl-2-pyrrolidone=30 grams (0.25 mole)
dimethylaminoethyl methacrylate=10 grams (0.063 mole)
 α -eicosene=160 grams (0.57 mole)
methyl *isobutylcarbinol*=150 grams
di-*t*-butyl peroxide=10 grams (initial)

The flask was then thoroughly purged with nitrogen and heated. A reaction temperature of 125°-135°C. was maintained for 16 hours and then 5.0 more grams peroxide was added and the reaction continued for another 16 hours. (Total peroxide=15 grams or 0.1 mole). After cooling, the contents were analyzed and found to contain no residual N-vinyl-2-pyrrolidone or the dimethylaminoethyl methacrylate and only 6.58% by weight as α -eicosene corresponding to 24 grams of the olefin. When the solvent was removed in high vacuum and substituted with 200 grams 100 Sec. Solv., a clear amber solution was obtained.

EXAMPLE VIII

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following materials were charged:

N-vinyl-2-piperidone=125 grams (1.0 mole)
 α -octadecene=252 grams (1.0 mole)
normal butanol=200 grams
di-*t*-butyl peroxide=14.6 grams (0.1 mole)

The flask was purged thoroughly with nitrogen and heated. The contents were maintained at reflux (120°C. pot) for 30 hours and then cooled and analyzed. The analyses showed the total absence of N-vinyl-2-piperidone and the presence of only 3.05%

of α -octadecene in the solution, corresponding to 18 grams unreacted olefin.

When all the solvent was stripped in vacuum and substituted with 377 grams 100 Sec. Solv., a very clear oily solution, weighing 750 grams (50%), was obtained.

EXAMPLE IX

Into a one-liter, four-necked reaction flask, equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following materials were charged:

N-vinyl- ϵ -caprolactam=139 grams (1.0 mole)
 α -octadecene=214 grams (0.85 mole)
methyl *isobutylcarbinol*=200 grams
di-*t*-butyl peroxide=13.1 grams (0.09 mole)

The flask was then purged thoroughly with nitrogen, heated and maintained at 125°-135°C. for 24 hours. The contents when analyzed showed the absence of N-vinyl- ϵ -caprolactam and the presence of 4.54% of the α -octadecene, corresponding to only 25.7 grams of the unreacted olefin. Then as the solvent was stripped in vacuum, 353 grams 100 Sec. Solv. was added and the product obtained as a 50% oil solution (705 grams).

EXAMPLE X

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following materials were charged:

N-vinyl-2-piperidone=70 grams (0.56 mole)
ethyl methacrylate=30 grams (0.26 mole)
 α -eicosene=252 grams (0.90 mole)
methyl *isobutylcarbinol*=200 grams
di-*t*-butyl peroxide=10 grams (0.68 mole)

The reaction flask was then thoroughly purged with nitrogen and heated. When the temperature reached 115°C. an exotherm was experienced, but the temperature was controlled and maintained at 125-135°C. After 8 hours, 10 more grams peroxide were added (total peroxide=20 grams, 0.137 mole) and heating continued for another 16 hours (total time=24 hours). The contents were then analyzed and found to contain neither N-vinyl-2-piperidone or ethyl methacrylate and only 5.75% unreacted α -eicosene, corresponding to 32.8 grams of the α -olefin. The solvent was then stripped in vacuum and substituted with 352 grams 100 Sec. Solv. The resulting 50% solution in oil was clear and weighed 700 grams.

EXAMPLE XI

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following materials were charged:

N-vinyl-2-pyrrolidone=111 grams (1.0 mole)
 α -decene=210 grams (1.5 mole)
normal butanol=200 grams
di-benzoyl peroxide=25 grams (0.1 mole)

After purging the system with nitrogen

the contents were heated and maintained at 95—100°C. for 10 hours. The solution was then analyzed and found to contain no residual N-vinyl-2-pyrrolidone and only 5 23.5% α -decene corresponding to 128 grams unreacted of α -decene. The contents were transferred into a flask, the solvent stripped in vacuum and then maintained at a bath temperature of 130—140°C. and 3—5 mm 10 Hg. for 24 hours. The clear colourless solid (188 grams) was analyzed and found to contain 7.45% nitrogen corresponding to 15 59% reacted N-vinyl pyrrolidone in the product. The product was hydrophobic and soluble in variety of organic solvents.

EXAMPLE XII

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following ingredients 20 were charged:

N-vinyl-2-pyrrolidone=55.5 grams (0.5 mole)
N-vinyl-3-morpholinone=63.5 grams (0.5 mole)
methyl isobutylcarbinol=200 grams
25 α -octadecene=315 grams (1.25 mole)
t-butyl hydroperoxide=11 grams (0.12 mole)

The flask was purged with nitrogen thoroughly and heated. The contents were maintained at 130—140°C. for 12 hours 30 and then 11.0 more grams of peroxide were added and heating continued for another 12 hours. (Total peroxide=22.0 grams or 0.24 mole). In analysis of the contents, no trace of N-vinyl-2-pyrrolidone or N-vinyl-3-morpholinone were found but only the presence of 11.6% of α -octadecene was detected 35 which indicates a residual of 76 grams unreacted olefin. The contents were then transferred into a two-liter flask and the solvent stripped in vacuum and substituted with 434 grams 100 Sec. Solv. The final 50% solution was a clear amber liquid weighing 850 grams.

EXAMPLE XIII

45. Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, after a thorough nitrogen purge, the following ingredients were charged and heated:

50 N-vinyl-5-methyl-2-pyrrolidone=125 grams (1.0 mole)
Hexanol (mixture of isomeric hexanoles)=200 grams
 α -octadecene=227 grams (0.9 mole)
55 di-t-butyl peroxide=15 grams (0.1 mole)

The solution was maintained at 120°—140°C. for 30 hours and then cooled and analyzed. It was found to contain less than 0.1% by weight of monomer and only 2.4% 60 α -octadecene, corresponding to 13.6 grams, or a 94% consumption of the α -olefin charged. When the solvent was removed in vacuum and substituted with 352 grams

100 Sec. Solv., a clear (50%) solution was obtained which weighed 700 grams (Theory= 704 grams). 65

EXAMPLE XIV

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, after a thorough nitrogen purge, the following ingredients were charged:

N-vinyl-2-oxazolidone=56.5 grams (0.5 mole)
methyl isobutylcarbinol=200 grams
 α -eicosene=210 grams (0.75 mole)
di-t-butyl peroxide=11.0 grams (0.075 mole)

The mixture was then heated and maintained at 120°—140°C. for 12 hours and then another 11.0 grams (total peroxide=22.0 grams, 0.15 mole) peroxide added and the reaction continued. After a total of 28 hours reaction period, the contents were cooled and analyzed. It was found to contain 0.2% by weight of N-vinyl oxazolidone (equivalent to 0.98 grams) and 3.44% of α -eicosene (equivalent to 16.8 grams) by weight of the solution. To form a 35% solution of the product in 100 Sec. Solv., the solvent was stripped in vacuum and at the same time 495 grams of the 100 Sec. Solv. was added. The final solution obtained was clear and weighed 760 grams. (Theory=761.5 grams).

EXAMPLE XV

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following ingredients were charged:

N-vinyl-3-morpholinone=63.5 grams (0.5 mole)
normal butanol=150 grams
 α -hexadecene=224 grams (1.0 mole)
di-t-butyl peroxide=15 grams (0.1 mole)

The flask was purged with nitrogen, heated and maintained at reflux (118°—124°C.) for 16 hours. Then another 7.0 grams peroxide was added (total peroxide=22.0 grams, 0.15 mole) and refluxing continued for 20 more hours (total=36 hours). The contents were then cooled and analyzed. It was found to contain 0.05% of N-vinyl-3-morpholinone (equivalent to 0.23 gram) and 4.7% α -hexadecene (equivalent to 21.6 grams unreacted by weight of solution). Then the solvent of the product-solution was stripped and the remainder subjected to high vacuum (0.05—1.0 mm. Hg.) and temperatures of up to 140°C. The residue obtained weighed 280 grams, and was clear, colourless and very viscous. This product was soluble in a variety of polar and non-polar organic solvents.

EXAMPLE XVI

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following ingredients were charged:

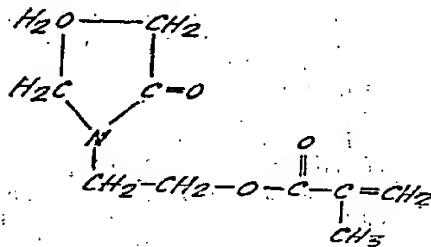
N-vinyl succinimide=62.5 grams (0.5 mole)
 Methyl isobutylcarbinol=150 grams
 α -eicosene=182 grams (0.65 mole)
 di-*t*-butyl peroxide=15 grams (0.1 mole)

5 The flask was purged with nitrogen, heated and maintained at a range of 120°—140°C. for 30 hours. The contents were then cooled and analyzed and found to contain only a trace of N-vinyl succinimide and 3.66% (equivalent to 15.0 grams unreacted only) of α -eicosene by weight of the solution. Then 244.5 grams of 100 Sec. Solv. was added and the solvent stripped in vacuum. The final 50% solution obtained was clear and weighed 15 485 grams. (Theory=489.0 grams).

EXAMPLE XVII

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, after a thorough nitrogen purge, the following ingredients were charged and heated:

20 N-methacryloyloxyethylpyrrolidone = 46.0 grams (0.23 mole)



25 N-butanol=200 grams
 α -eicosene=140 grams (0.5 mole)
 di-*t*-butyl peroxide=10 grams

The mixture (clear phase) was maintained at reflux (117—125°C.) for 20 hours and 30 then another 5.0 grams peroxide added (total peroxide=15.0 grams, 0.1 mole) and refluxing continued for 16 more hours. The contents were then cooled and analyzed. The analysis showed the total absence of the methacrylate and only 3.0% (equivalent to 12.0 grams unreacted) of α -eicosene. The solvent was then stripped in vacuum and substituted with 186 grams 100 Sec. Solv. The final 50% solution in the 100 Sec. Solv. 40 Solvent was clear and weighed 371 grams. (Theory=372 grams).

EXAMPLE XVIII

N-vinyl-2-pyrrolidone (111 grams, 1 mole) was dissolved in 250 grams of anhydrous ethanol and then 14.6 grams (0.1 mole) of di-*t*-butyl peroxide added and the solution transferred into a one-liter stainless steel rocker bomb. Chlorotrifluoroethylene ($CCl=CF_2$) 60.0 grams (0.51 mole) was then charged into the bomb and the bomb heated and maintained at 125°—130°C. for

24 hours. After cooling the contents were discharged into a one-liter four-necked flask and subjected to vacuum distillation to remove solvent and light boiling components. The dry solid obtained as residue analyzed for 13.3% of fluorine and 7.7% of chlorine corresponding to 27% of the chlorotrifluoroethane by weight of the product.

EXAMPLE XIX

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following materials were charged:

N-vinyl-2-pyrrolidone=112.21 grams (1.0 mole)

α -octene=112.21 grams (1.0 mole)

normal butanol=200 grams

di-*t*-butyl peroxide=14.6 grams (0.1 mole)

The flask was purged thoroughly with nitrogen and heated. The contents were maintained at reflux for 30 hours and then cooled and analyzed. The analysis showed the total absence of N-vinyl-2-pyrrolidone and the presence of only 3% of α -octene in the solution corresponding to 13.13 grams of unreacted olefin.

When all the solvent was stripped in vacuum and substituted with 450 grams of 100 Sec. Solv., a very clear oily solution, weighing 674 grams (50%), was obtained.

EXAMPLE XX

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following materials were charged:

N-vinyl-2-pyrrolidone=55.5 grams (0.5 mole)

C_{12} α -olefin obtained by the trimerization of

α -tetradecene=294 grams (0.5 mole)

methyl isobutylcarbinol=120 grams

di-*t*-butyl peroxide=15 grams (0.1 mole)

The flask was purged thoroughly with nitrogen and heated. The contents were maintained at reflux for 24 hours and then cooled and analyzed. The analysis showed the total absence of N-vinyl-2-pyrrolidone and the presence of 7.75% of the C_{12} α -olefin in the solution corresponding to 37.5 grams of unreacted olefin.

When all the solvent was stripped in vacuum and substituted with 349 grams of 100 Sec. Solv., a clear amber coloured oily solution, weighing 695 grams (50%), was obtained. The solution solidifies on cooling to an amber colored wax, but reverts to the liquid phase on warming.

From the foregoing specification and illustrative working examples it becomes clearly evident that by the simultaneous polymerization and alkylation process of the present invention the solubility of the polymers, homo- and co-polymers, can be systematically controlled, both by the type of α -olefin

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used and the amount thereof, so that polymers which are still soluble in polar solvents, such as alcohols to polymers which are soluble in aliphatic hydrocarbons, mineral and lubricating oils can be obtained as well as polymers having intermediate degrees of solubility between polar and non-polar solvents. Thus, polymers with a low degree of alkylation are still soluble in ethanol, so that they can be formulated with "Freons" as aerosol hair sprays, but their sensitivity to moisture is reduced. "Freon" is a Trade Mark. These polymers can also be formulated into adhesives with superior properties because of their increased resistance to moisture. Polymers with a high degree of alkylation are soluble in hydrocarbon liquids and liquid petroleum products. When dissolved in kerosenes, jet fuels, furnace oils and similar combustible liquids at a concentration from about 0.001% to 2% by weight, they provide effective protection against deposition or separation of gums, resins and sludges. They are effectively useful as viscosity index improvers and as gum resin and sludge dispersants in lubricating oils. When dissolved in lubricating oils at a concentration from about 0.03% to 5% by weight they readily disperse gums, resins and sludges which may form and thus prevent their deposition on engine parts. The homopolymer and copolymer alkylates of α -olefins of from 8 to 42 carbon atoms are a new class of products and are especially useful as dispersants for engine oils since they leave no deposit, i.e., they are ashless. Polymers with a high degree of alkylation are soluble in hydrocarbon polymers such as polyethylene and polypropylene and impart dye receptivity to these difficultly dyed polymers. When employing α -olefins of from 2 to 4 carbon atoms during the homo- or co-polymerization, polymers are obtained which are more flexible and less tacky under high humidity conditions than PVP itself or vinyl pyrrolidone vinyl acetate copolymers. The flexibility increases and the tack at high humidity decreases as the per cent alkylate increases. While the present invention has been described in detail with respect to the simultaneous polymerization and alkylation of individual heterocyclic N-vinyl monomers, mixtures thereof, and a mixture of a heterocyclic N-vinyl monomer and a non-heterocyclic polymerizable monoethylenically unsaturated monomer, we found during the experimentation therewith that alkylated graft polymers are readily prepared by first copolymerizing 0.1 to 0.5 moles of a mixture of two non-heterocyclic polymerizable monoethylenically unsaturated monomers until about 50% thereof has been polymerized and then continuing the polymerization and alkylation by the addition of 0.5 to 0.9 mole of a heterocyclic N-vinyl monomer and 0.05 to 12 moles of an α -olefin of at least 8 carbon atoms until alkylation and polymerization are complete. Illustrative of such class of non-heterocyclic polymerizable monoethylenically unsaturated monomers, methyl methacrylate, n-butyl methacrylate, lauryl methacrylate, stearyl methacrylate, vinyl stearate, dodecyl acrylate, may be mentioned. The proportions of such monomers in the mixture is not critical and may range from as low as 1% to 99% by weight of any non-heterocyclic polymerizable monoethylenically unsaturated monomer having a straight or branched chain alkyl group of from 1 to 18 carbon atoms and from 99% to 1% of another monomer containing an Alkyl group of from 1 to 18 carbon atoms.

The graft polymers are also useful as additives to petroleum fuels and lubricants. When dissolved in an amount ranging from 0.01 to 2% by weight in a fuel oil such as jet fuel, furnace oils, they inhibit the deposition or separation of gum, resins and sludges. When dissolved in lubricating oils in an amount ranging from 0.02 to 5% by weight, they are effective dispersing agents for gums, resins and sludges which may form and thus prevent their deposition on engine parts.

The homopolymer and copolymer alkylates of chloro-fluoro- α -olefin and fluoro- α -olefin of 2 carbon atoms are also a new and useful class of products having fire-retardant properties. They are especially useful in the formulation of fire-retardant adhesives, i.e., bonding agents for paper, plastics and textile fabrics. From solutions in a variety of organic solvents or as emulsions, the polymers form smooth continuous films which make them particularly useful as fire-retardant pre-coating agents for polyester laminates.

WHAT WE CLAIM IS:—

1. A process of simultaneously polymerizing and alkylating heterocyclic N-vinyl monomers which comprises heating one mole of a heterocyclic N-vinyl monomer, or one mole of a mixture of two such monomers, or one mole of a mixture of monomers containing from 5% to 99% by weight of a heterocyclic N-vinyl monomer and from 1% to 95% by weight of a non-heterocyclic polymerizable monoethylenically unsaturated monomer with 0.05 to 12 moles of an α -olefin chosen from chloro-fluoro- α -olefins and fluoro- α -olefins both containing 2 carbon atoms and an α -olefin containing at least 2 carbon atoms in an organic solvent common to all the above monomers, and the said α -olefins in the presence of 0.025 to 0.30 mole of an organic peroxide catalyst per mole of the said α -olefin at a temperature ranging from 80° to 200°C.

2. A process according to Claim 1, where-
in the heterocyclic N-vinyl monomer is an N-
vinyl lactam. 65

3. A process according to Claim 1, where-
5 in the heterocyclic N-vinyl monomer is N-
vinyl-2-pyrrolidone. 70

4. A process according to Claim 1, where-
in the heterocyclic N-vinyl monomer is N-
vinyl-5-methyl-2-pyrrolidone. 75

10 5. A process according to Claim 1, where-
in the heterocyclic N-vinyl monomer is N-
vinyl-2-piperidone. 75

6. A process according to Claim 1, where-
15 in the heterocyclic N-vinyl monomer is N-
vinyl- ϵ -caprolactam. 80

7. A process according to Claim 1, where-
in the heterocyclic N-vinyl monomer is N-
vinyl-2-oxazolidone. 80

20 8. A process according to Claim 1, where-
in the heterocyclic N-vinyl monomer is N-
vinyl-3-morpholinone. 85

9. A process according to Claim 1, where-
in the heterocyclic N-vinyl monomer is N-
vinyl succinimide. 90

25 10. A process according to Claim 1, where-
in there is used a mixture of monomers con-
sisting of 5% to 99% by weight of an N-
vinyl lactam and from 1% to 95% by weight
of vinyl acetate. 95

30 11. A process of simultaneously poly-
merizing and alkylating a comonomeric mix-
ture consisting of 47% by weight of N-
vinyl-2-pyrrolidone and 53% by weight of
N-vinyl-3-morpholinone which comprises
35 heating one mole of the said comonomeric
mixture with 1.25 moles of α -octadecene in
solution of methyl isobutylcarbinol in the
presence of 0.12 mole of *t*-butyl hydro-
peroxide at a temperature of 130°—140°C. 100

40 12. A process of simultaneously polymeriz-
ing and alkylating N-vinyl-2-pyrrolidone
which comprises heating one mole of the
said pyrrolidone with 0.5 mole of α -eicosene
in solution of methyl isobutylcarbinol in the
presence of 0.05 mole of di-*t*-butyl peroxide
45 at a temperature of 120°—135°C. 105

13. A process of simultaneously polymeriz-
ing and alkylating N-vinyl-5-methyl-2-
50 pyrrolidone which comprises heating one mole
of the said pyrrolidone with 0.9 mole of
 α -octadecene in solution of hexanol in the
presence of 0.1 mole of di-*t*-butyl peroxide
at a temperature of 120°—140°C. 105

55 14. A process of simultaneously polymeriz-
ing and alkylating N-vinyl-2-pyrrolidone
which comprises heating one mole of the
said pyrrolidone with 1.5 moles of α -decene
in solution of *n*-butanol in the presence of
60 0.2 mole of di-benzoyl peroxide at a
temperature of 95°—100°C. 105

15. A process of simultaneously polymeriz-
ing and alkylating N-vinyl-2-piperidone
which comprises heating one mole of the
said piperidone with 1 mole of α -octadecene
in solution of *n*-butanol in the presence
65 of 0.1 mole of di-*t*-butyl peroxide at a pot
temperature of 120°C. 65

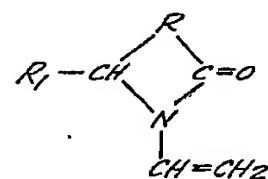
16. A process of simultaneously polymeriz-
ing and alkylating N-vinyl- ϵ -caprolactam
which comprises heating one mole of the
said caprolactam with 0.85 mole of α -
octadecene in solution of methyl isobutyl-
carbinol in the presence of 0.09 mole of di-
t-butyl peroxide at a temperature of 125° to
75 135°C. 75

17. A process of simultaneously polymeriz-
ing and alkylating N-vinyl-2-oxazolidone
which comprises heating one mole of the
said oxazolidone with 1.5 mole of α -eicosene
in solution of methyl isobutylcarbinol in
the presence of 0.3 mole of di-*t*-butyl per-
oxide at a temperature of 120°C to 140°C. 80

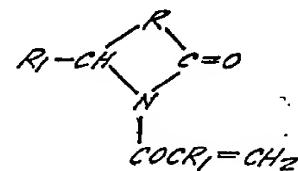
18. A process of simultaneously polymeriz-
ing and alkylating N-vinyl-3-morpholinone
which comprises heating one mole of the
said morpholinone with 2 moles of α -hexa-
decene in solution of *n*-butanol in the pres-
ence of 0.2 mole of di-*t*-butyl peroxide at a
temperature of 118° to 124°C. 85

19. A process of simultaneously polymeriz-
ing and alkylating N-vinyl succinimide which
comprises heating one mole of the said
succinimide with 1.3 moles of α -eicosene in
solution of methyl isobutylcarbinol in the
presence of 0.2 mole of di-*t*-butyl peroxide
at a temperature of 120° to 140°C. 90

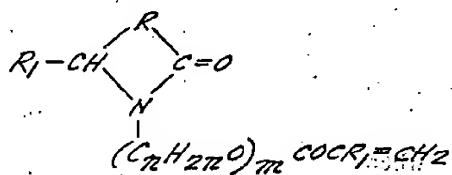
20. A process according to Claim 1, where-
in the heterocyclic N-vinyl monomer is
chosen from N-vinyl-2-oxazolidone, N-vinyl-
3-morpholinone, N-vinyl succinimide, N-
vinyl piperidine, N-vinyl diglycolylimide, N-
vinyl glutarimide, and monomers of the
following general formulae: 95



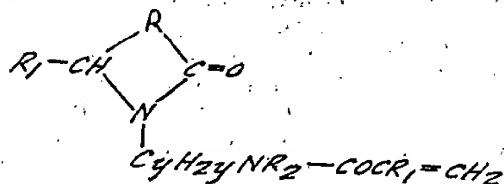
1)



2)



3)
and



4)
5) wherein R represents an alkylene bridge
of from 2 to 4 carbon atoms inclusive to
complete a 5-, 6- and 7-membered hetero-

cyclic ring system, R₁ is hydrogen or methyl,
R₂ is hydrogen, alkyl of from 1 to 12 carbon
atoms inclusive or phenyl, m is an integer of
from 1 to 4 inclusive, n is an integer of
from 1 to 4 inclusive when m has a value of
1 and of 2 to 4 inclusive when m has a value
greater than 1, and wherein y is 2 or 3.

10

21. A process according to any preceding
claim substantially as herein described and
exemplified.

15

22. An alkylated polymer obtained by the
process claimed in any preceding claim.

20

23. A copolymer of two different hetero-
cyclic N-vinyl lactams, in which some or
all of the heterocyclic rings contain one or
more alkyl groups of at least two carbon
atoms.

MEWBURN ELLIS & CO.,
Chartered Patent Agents,
70 & 72, Chancery Lane,
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Agents for the Applicants.

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